

The submillimeter spectrum of deuterated glycolaldehydes

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ABSTRACT

Context. Glycolaldehyde, a sugar-related interstellar prebiotic molecule, has recently been detected in two star-forming regions, Sgr B2(N) and G31.41+0.31. The detection of this new species increased the list of complex organic molecules detected in the interstellar medium (ISM) and adds another level to the chemical complexity present in space. Besides, this kind of organic molecule is important because it is directly linked to the origin of life. For many years, astronomers have been struggling to understand the origin of this high chemical complexity in the ISM. The study of deuteration may provide crucial hints.

Aims. In this context, we have measured the spectra of deuterated isotopologues of glycolaldehyde in the laboratory: the three mono-deuterated ones ($\text{CH}_2\text{OD-CHO}$, CHDOH-CHO and $\text{CH}_2\text{OH-CDO}$) and one dideuterated derivative (CHDOH-CDO) in the ground vibrational state.

Methods. Previous laboratory work on the D-isotopologues of glycolaldehyde was restricted to less than 26 GHz. We used a solid-state submillimeter-wave spectrometer in Lille with an accuracy for isolated lines better than 30 kHz to acquire new spectroscopic data between 150 and 630 GHz and employed the ASFIT and SPCAT programs for analysis.

Results. We measured around 900 new lines for each isotopologue and determined spectroscopic parameters. This allows an accurate prediction in the ALMA range up to 850 GHz.

Conclusions. This treatment meets the needs for a first astrophysical research, for which we provide an appropriate set of predictions.

Key words. ISM : molecules, line identification, methods : laboratory, Deuterated glycolaldehyde, isotopologues, millimeter-wave, radio-astronomy.

1. Introduction

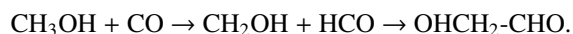
A search for various major isotopologues of key species in the interstellar medium (ISM) is still hampered by a scarcity of reliable spectroscopic data from laboratory measurements, which has also been the case for deuterated glycolaldehyde. However, studying the spectra and abundances of isotopologues in the ISM can be a valuable tool in chemical and physical modelling. In particular, a study of the isotopologues of known organic molecules can provide information for understanding molecular complexity in star-forming regions (SFRs). The detection of deuterated molecules has a strong impact for understanding and modelling the formation and deuteration process of molecules. This is especially interesting for complex molecules for which it may allow differentiating the gas-phase and solid-state formation pathways.

Glycolaldehyde is the smallest possible molecule that contains both an aldehyde group and a hydroxyl group and this dimer of formaldehyde can be considered as the simplest sugar. It is an isomer of methyl formate (HCOOCH_3) and acetic acid (CH_3COOH), and the relative abundance of these isomers are two of the three exceptions of the minimum energy principle (Lattalais et al. 2009); the most stable isomer, acetic acid, should be the most abundant, but in all astronomical sources where it was searched for, methyl formate is much more abundant, and

acetic acid and glycolaldehyde have about the same abundance. These exceptions could be due to the kinetic or abundance effect, or to the existence of different routes of formation with no intermediate in common or to specific depletion on the grains of one isomer with respect to the others.

Glycolaldehyde is a probable prebiotic molecule and a key intermediate in the formose reaction, i.e the formation from formaldehyde of sugars containing three, four, or five C-atoms. It has been detected in the star-forming region Sgr B2(N) by Hollis et al. (2000) from 2 and 3 mm single-dish surveys, with an estimated rotational temperature (T_{rot}) of 35K from 34 lines detected. Beltrán et al. (2009) reported identification of three lines towards the hot core G31.41 +0.31 using the Plateau de Bure Interferometer. Their analysis indicated that emission comes from the hottest ($\geq 300\text{K}$) and the densest ($\geq 2 \times 10^8 \text{ cm}^{-3}$) region closest to the protostar. Although some transitions of the parent molecule have been observed, no investigation of the isotopologues has yet been reported because of (i) the lack of spectroscopic data and (ii) the expected weakness of their emission. However, observations like this would help us to understand the formation pathway of the parent molecules, which is currently unclear. Indeed, several gas-phase and solid-phase routes of formation of glycolaldehyde have been proposed. The possible gas-phase pathway is the formose reaction (Jalbout et al. 2007): protonated formaldehyde CH_2OH^+ can re-

act with formaldehyde to yield glycolaldehyde. However, a recent study by Simakov et al. (2011) compromises this formation route: the authors reported that protonated formaldehyde does not lead to protonated glycolaldehyde. Other recent studies (e.g. Hamberg et al. 2010) have shown that dissociative recombination reactions of a protonated molecule HX^+ do not lead to the stable molecule X for the most part. Hence a more probable route of formation is via the reaction of methanol and carbon monoxide on interstellar ices (Bennett & Kaiser 2007):



To date, no identification of the deuterio-isotopologues has been reported, but a comparison of D/H ratios may be valuable for understanding the formation of glycolaldehyde. Indeed, in hot cores and hot corinos the deuteration fraction of complex organic molecules is much greater than the cosmic D/H ratio (10^{-5} ; Oliveira & Hébrard, 2006) because it is around 10^{-3} . This ratio is more studied in hot corinos where the process of deuteration is considered to be overabundant (detected molecules can be doubly or triply deuterated, as described for example by Ceccarelli et al. (1998)). This is used to determine the formation pathway as shown by Cazaux et al. (2011) and Coutens et al. (2011), with the formation of water and formaldehyde. However, the process could be similar for hot cores, as shown by Turner (1990) or recently by Ratajczak et al. (2011). Therefore we recently made extensive laboratory measurements to be able to search for the millimeter-wave spectrum of D-isotopologues of glycolaldehyde in the ISM. These measurements are particularly relevant to ALMA because of its high sensitivity and high spatial resolution (that could, for example, reduce the spectral line confusion). However, it might also be possible to identify these isotopologues using sensitive single-dish instruments such as the IRAM-30m.

The first microwave spectrum measurements of the main isotopologue of glycolaldehyde were reported by Marstokk & Møllendal (1970), who obtained the pure rotational and centrifugal distortion constants of the ground state and three vibrational excited states, as well. In addition, in 1973 they were able to determine the electric dipole moment as $\mu_b = 2.33$ D and $\mu_a = 0.26$ D. Then Butler et al. (2001) extended millimeter and submillimeter assignments for the ground vibrational state from 128 to 354 GHz. A subsequent study by Widicus Weaver et al. (2005) included assignments for the ground state and three excited vibrational states up to 354 GHz as well as a partition function analysis. Finally, Carroll et al. (2010) reported the spectrum of the ground vibrational state in selected regions of the submillimeter region up to 1.2 THz. Less information is available on the other isotopologues of glycolaldehyde. The only published measurements for the deuterium isotopologues are from Marstokk & Møllendal (1971), whose measurements were restricted to between 12 and 26 GHz. Considering the importance of understanding the formation of this molecule and the development of (sub)millimeter observatories, new data are needed, which is why we measured the spectra of all mono-deuterated isotopologues ($CH_2OD-CHO$, $CHDOH-CHO$, $CH_2OH-CDO$, cf. figure 1) of glycolaldehyde and one doubly deuterated one ($CHDOH-CDO$, cf. figure 1) between 150 and 630 GHz in the laboratory.

2. Experiments

The submillimeter-wave measurements (150-630 GHz) were performed using the Lille spectrometer (Motiyenko et al., 2010)

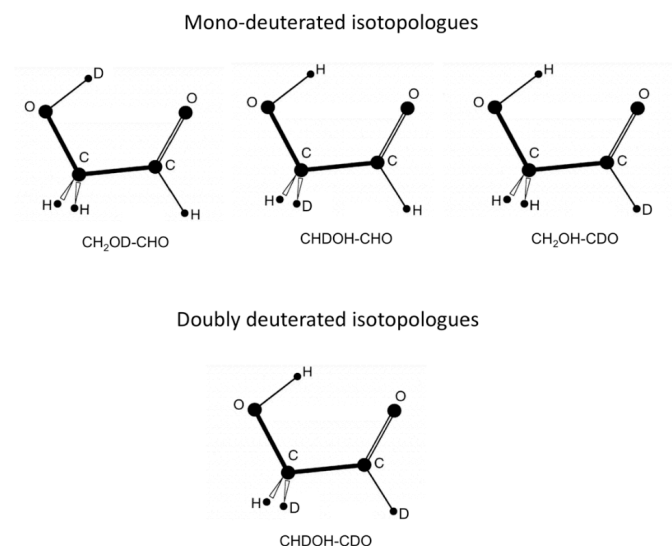


Fig. 1. Representation of all mono-deuterated isotopologues of glycolaldehyde and the doubly deuterated one.

based only on solid-state sources. The frequency of an Agilent synthesizer E8257D (12.5-17.5 GHz) was first multiplied by six and amplified by a Spacek active sextupler, providing an output power of +15dBm in the W-band range (75-110 GHz). This power is high enough to use passive Schottky multipliers (x2, x3, x5, x3x2) from Virginia Diodes Inc in the next stage of the frequency multiplication chain. As a detector we used an InSb liquid He-cooled bolometer from QMC Instruments Ltd. To improve the sensitivity of the spectrometer, the sources were frequency modulated at 10 kHz and phase-sensitive detection at 2f was employed. The absorption cell is a stainless-steel tube (6 cm diameter, 220 cm long). The sample pressure during measurements was about 1.5 Pa (15 μ bar) and the linewidth was limited by Doppler broadening. Measurements were performed at room temperature. The accuracy of the measurements for isolated lines is estimated to be better than 30 kHz. However, if the lines were blended or had a poor signal-to-noise ratio, they were given a weight of 100 or even 200 kHz.

The synthesis procedure was as follows:

Synthesis of deuterated glycolaldehydes: 1,4-Dioxane-2,5-diol and dihydroxyfumaric acid hydrate were purchased from Aldrich and used without additional purification.

Synthesis of $DOCH_2CHO$: 1,4-Dioxane-2,5-diol (5 g) was dissolved in deuterated water (10 mL) and heated to 70°C for 1h. The mixture was lyophilised to obtain a solid sample of $DOCH_2CHO$ with about 25% isotopic purity.

Synthesis of $HOCHD-CHO$, $HOCH_2-CDO$ and $HOCHD-CDO$: The synthesis reported by Marstokk & Møllendal (1973) was used starting from dihydroxyfumaric acid hydrate dissolved in about 80% D_2O . Decarboxylation in dry pyridine as described by Powers et al. gave an about 2:1:1 mixture of $HOCHD-CHO$, $HOCH_2-CDO$ and $HOCHD-CDO$. Small amounts of residual pyridine, a compound more volatile than glycolaldehyde, led to relatively intense signals in the microwave spectrum.

3. Analysis

Glycolaldehyde is a prolate asymmetric top molecule ($\kappa = -0.7$). Therefore we used the Watson A-reduction

Hamiltonian in the I'' representation in the analysis of its spectra. Spectral data were fitted using the ASFIT programme¹. Predictions were made using the SPCAT programme (Pickett et al. (1998)) and the parameter set resulting from ASFIT and the dipole moments determined by Marstokk & Møllendal (1973).

The first species measured and analysed was DOCH₂CHO with the enriched sample containing only this isotopologue and the parent species with an estimated proportion of 25% of OD as shown in figure 2.

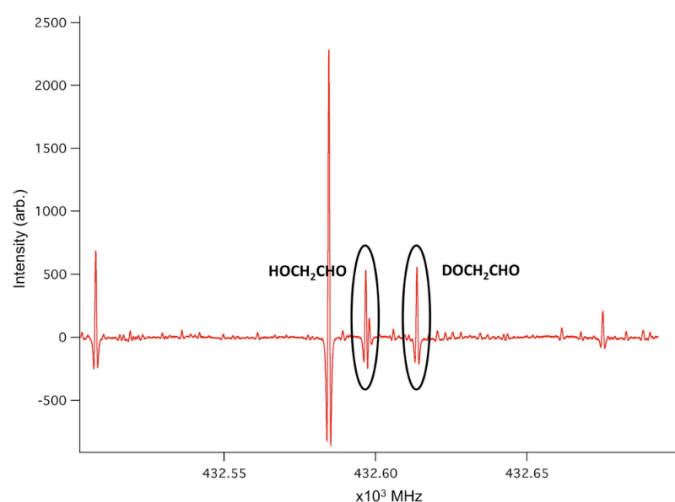


Fig. 2. Part of the spectrum of the first sample containing HOCH₂CHO (transition 39_{7,32}-38_{8,31} and intensity $\alpha=1.37 \cdot 10^{-4} \text{ cm}^{-1}$) in the first excited vibrational state and DOCH₂CHO (transition 38_{7,32}-37_{6,31} and intensity $\alpha=5.83 \cdot 10^{-4} \text{ cm}^{-1}$).

Initial predictions were made using lines reported in Marstokk & Møllendal (1971) between 12 and 26 GHz. First, we identified the strong R-branch transitions with $K_a = 0$ and 1 between 150 and 310 GHz up to $J=31$. The low J lines were easily recognised doublets (K_a selection rules: 1-0 & 0-1) with systematic decrease in the split towards higher J and visible addition of the intensities as the components merge. All transitions were shifted systematically from the predictions up to a maximum of around 10 MHz at $J = 20$. The newly identified lines were then included in the fit. Next we identified lines by systematically increasing K_a up to $K'_a=11$ and finally measured all other identifiable R-branch lines (up to $J=59$ and $K'_a=18$). We then identified three Q branches and assigned all lines possible. The same procedure was then repeated for a second frequency band between 400 and 630 GHz. Finally, we assigned some P-branch transitions. Since these lines were much weaker, assignment was only possible in the region around 300 GHz where the spectrometer is most sensitive. Because the strong b -component of the dipole moment (2.33 D) is much stronger than the a -component (0.26 D), all newly assigned lines are b -type transitions.

To check the relative weight of the Lille and centimeterwave data sets, the method of iteratively reweighted least-squares (IRLSQ) of Margules et al. (2010) was used. As a result, 63 of the 65 lines from Marstokk & Møllendal (1971) were rejected from the fit. We found a systematic deviation of 150 kHz for these measurements, and consequently they were ex-

cluded from the final fit. The same kind of deviation was also found for the data on other deuterated species available from Marstokk & Møllendal (1971). The final fit is given in the supplementary Table 2. It contains 889 new identified lines (1433 transitions, because there are 355 unresolved doublets and 63 quadruplets) up to $J = 64$ and $K'_a = 37$.

We were able to determine all sextic centrifugal distortion parameters. Including some octic parameters made no significant improvement and consequently they were excluded from the final fit. The rms deviation of the fit is 27 kHz with a weighted rms of 0.90, which indicates that the experimental uncertainty was correctly estimated. Table 1 gives the rotational and centrifugal distortion parameters.

The second studied sample contained the three isotopologues CHDOH-CHO, CH₂OH-CDO, and CHDOH-CDO with an abundance ratio of 2 : 1 : 1. The analysis was carried out for each isotopologue independently, as previously described for CH₂ODCHO, and all newly assigned lines are b -type transitions, too. However, the analysis was complicated by the presence of three different isotopologues and the presence of many pyridine lines resulting from the synthesis procedure.

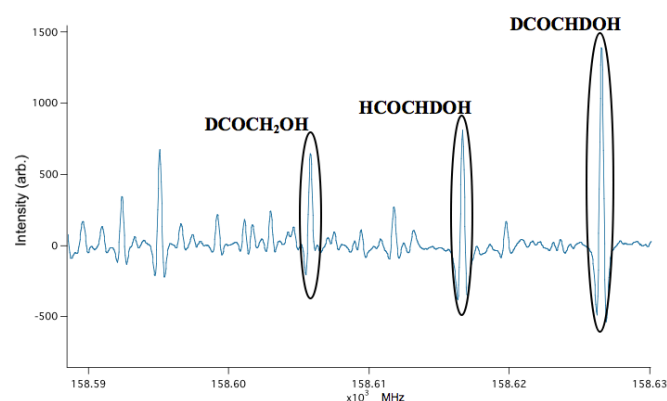


Fig. 3. Part of the spectrum of the second sample containing CHDOH-CHO (transition 23_{3,20}-23_{2,21} and intensity $\alpha=1.62 \cdot 10^{-4} \text{ cm}^{-1}$), CH₂OH-CDO (transition 7_{4,3}-6_{3,4} and intensity $\alpha=1.90 \cdot 10^{-4} \text{ cm}^{-1}$) and CHDOH-CDO (transition 33_{10,23}-33_{9,22} and intensity $\alpha=2.01 \cdot 10^{-4} \text{ cm}^{-1}$).

For CHDOH-CHO a total of 945 new lines were identified (1340 transitions because there are 179 unresolved doublets and 72 quadruplets) up to $J = 64$ and $K'_a = 27$.

For CHDOH-CDO we obtained 916 new identified lines (1368 transitions because there are 197 unresolved doublets and 85 quadruplets) up to $J = 67$ and $K'_a = 29$.

Finally for CH₂OH-CDO we obtained 858 new identified lines (1268 transitions because there are 203 unresolved doublets and 69 quadruplets) up to $J = 65$ and $K'_a = 24$.

Table 1 gives the rotational and centrifugal distortion parameters determined for these three other isotopologues. We used the same parameter set for each isotopologue that was determined by trial as best (i.e, lowest rms with minimal number of parameters). All quartic and sextic centrifugal terms were determined. The uncertainties on the parameters and the weighted rms of the fits (0.87, 0.87 and 0.90 for CHDOH-CHO, CHDOH-CDO, CH₂OH-CDO respectively) are similar for all isotopologues.

¹ Kisiel, PROSPE, <http://www.ifpan.edu.pl/~kisiel/prospe.htm>

Table 1. Determined rotational and centrifugal distortion parameters.

Parameters	CH ₂ OD-CHO	CHDOH-CHO	CHDOH-CDO	CH ₂ OH-CDO
A /MHz	17490.68230 (18)	16987.80362 (18)	15862.45361 (17)	17150.99706 (21)
B /MHz	6499.72649 (12)	6385.430683 (91)	6233.230843 (90)	6362.87482 (10)
C /MHz	4882.948293 (76)	4843.811766 (70)	4663.584048 (65)	4778.922377 (73)
Δ_J /kHz	6.349256 (81)	5.622519 (55)	4.988629 (52)	5.471924 (59)
Δ_{JK} /kHz	-17.93851 (31)	-15.51877 (26)	-13.56931 (22)	-16.70029 (31)
Δ_K /kHz	37.67004 (34)	35.90235 (46)	28.82809 (37)	36.52446 (81)
δ_J /kHz	1.898798 (40)	1.656979 (23)	1.508496 (23)	1.650572 (26)
δ_K /kHz	8.81685 (86)	7.59317 (44)	6.10186 (36)	7.30024 (46)
Φ_J /mHz	-0.008080 (30)	-0.006612 (17)	-0.005815 (16)	-0.006307 (18)
Φ_{JK} /Hz	0.15452 (42)	0.13274 (27)	0.10725 (21)	0.12995 (28)
Φ_{KJ} /Hz	-0.6494 (15)	-0.5728 (10)	-0.43733 (80)	-0.5700 (10)
Φ_K /Hz	0.7573 (12)	0.71373 (86)	0.50818 (67)	0.7048 (12)
ϕ_J /mHz	-0.002662 (15)	-0.0022434 (84)	-0.0020597 (82)	-0.0021147 (88)
ϕ_{JK} /mHz	-0.03007 (40)	-0.02255 (23)	-0.01534 (19)	-0.01999 (22)
ϕ_K /Hz	0.2636 (47)	0.1945 (29)	0.1254 (21)	0.1777 (26)
J_{MAX}, K_{aMAX}	64, 37	64, 27	67, 29	65, 24
Freq _{MAX} /MHz	626777.73	629356.35	626675.43	623233.58
nbr of transitions	889	945	916	858
σ_{FIT} /kHz	27	26	26	27

A full list of measurements is given in Tables 2, 3, 4 and 5 for CH₂OD-CHO, CHDOH-CHO, CH₂OH-CDO, and CHDOH-CDO, respectively. These tables give the rotational quantum numbers, the observed frequencies, the residuals (obs-cal), and the assumed experimental uncertainties. Blended transitions are treated by fitting the intensity-averaged frequency, and this weighting is also given in the tables. Lines with obvious experimental problems are not included. (Only the first 12 lines of Table 2 appear in the paper edition; for a complete version of all species, see the electronic edition or <http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/A+A/Vol/Num>)

4. Conclusion

The rotational spectra of three mono-deuterated glycolaldehyde isotopologues and a doubly deuterated one in the ground vibrational state have been characterised up to 630 GHz. This frequency range is appropriate for a first astronomical identification. Most importantly for an astrophysical research, the new measurements provide complete and precise predictions in the range of one to several hundred GHz, which is the optimum range for detection, taking into account the supposed temperature (≥ 35 K see introduction) and instrumental sensitivity. It is essential to be able to search for transitions over a wide frequency range not only to confirm the detection, but also because of spectral cluttering from other species. The measurements at higher frequency ensure the reliability of the predictions, but may also be useful in their own right, especially if glycolaldehyde should be detected at higher temperatures. The increased sensitivity provided by a new generation of radio-astronomical instruments (e.g., upgrading at the IRAM-30m) and by new facilities such as the ALMA interferometer renders the prospect of detecting new deuterated isotopologues in astrophysical environments a realistic one. Using the recently measured data, we have therefore started to search for deuterated glycolaldehyde in existing spectral surveys of hot-core sources and plan new observations.

(PCMI-CNRS) and J.-C. G. thanks the Centre National d'Etudes Spatiales (CNES) for financial support. We would like to thank the referee for his/her useful comments about the fits.

References

- Beltrán, M. T., Codella, C., Viti, S., Neri, R., & Cesaroni, R. 2009, *ApJ*, 690, L93
- Beltrán, M. T., Cesaroni, R., Neri, R., et al. 2005, *A&A*, 435, 901
- Bennett, C. J., & Kaiser, R. I. 2007, *ApJ*, 661, 899
- Butler, R. A. H., De Lucia, F. C., Petkie, D. T., et al. 2001, *ApJS*, 134, 319
- Carroll, P. B., Drouin, B. J., & Widicus Weaver, S. L. 2010, *ApJ*, 723, 845
- Cazaux, S., Caselli, P., & Spaans, M. 2011, *ApJ*, 741, L34
- Ceccarelli, C.; Castets, J.; Loinard, L.; Caux, E. and Tielens, A.G.G.M. 1998 *A & A*, 338, L43
- Coutens A., Vastel C., Caux E. et al. 2011, *A & A* in press
- Hollis, J. M., Lovas, F. J., & Jewell, P. R. 2000, *ApJ*, 540, L107
- Halfen, D. T., Apponi, A. J., Woolf, N., Polt, R., & Ziurys, L. M. 2006, *ApJ*, 639, 237
- Hamberg, M., Österdahl, F., Thomas, R. D., et al. 2010, *A&A*, 514, A83
- Jalbout, A. F., Abrell, L., Adamowicz, L., et al. 2007, *Astrobiology*, 7, 433
- Lattalais, M., Pauzat, F., Ellinger, Y., & Ceccarelli, C. 2009, *ApJ*, 696, L133
- Margulès, L., Motiyenko, R. A., Alekseev, E. A., & Demaison, J. 2010, *J. Mol. Spectrosc.*, 260, 23
- Marstokk, K., & Møllendal, H. 1970, *J. Mol. Struct.*, 5, 205
- Marstokk, K. & Møllendal, H. 1971, *J. Mol. Struct.*, 7, 101
- Marstokk, K., & Møllendal, H. 1973, *J. Mol. Struct.*, 16, 259
- Mauersberger, R., Henkel, C., Jacq, T., & Walmsley, C. M. 1988, *A&A*, 194, L1
- Motiyenko, R. A., Margulès, L., Alekseev, E. A., Guillemin, J. C., & Demaison, J. 2010, *J. Mol. Spectrosc.*, 264, 94
- Oliveira C. & Hébrard G. 2006, *ApJ*, 653, 345
- Parise, B.; Ceccarelli, C.; Tielens, A. G. G. M. et al. 2002 *A & A*, 393, L49
- Parise, B.; Castets, A.; Herbst, E. et al. 2004, *A & A* 416, 159
- Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, *J. Quant. Spec. Radiat. Transf.*, 60, 883
- Ratajczak, A., Taquet, V., Kahane, C., et al. 2011, *A&A*, 528, L13
- Simakov, A., Sekiguchi, O., Bunkan, A., Joakim C., Uggerud, E., 2011, *J. Am. Chem. Soc.*, 133, 20816-20822
- Turner, B. E. 1990, *ApJ*, 362, L29
- Widicus Weaver, S. L., Butler, R. A. H., Drouin, B. J., et al. 2005, *ApJS*, 158, 188

Acknowledgements. This work is supported by the contract ANR-08-BLAN-0225 and by the Programme National de Physico-Chimie du Milieu Interstellaire

Table 2. Assigned transitions for the ground state of CH₂OD-CHO.

J'	K' _a	K' _c	J''	K'' _a	K'' _c	Frequency (MHz)	Obs. - Calc. (MHz)	Uncertainty (MHz)	Intensity weighting for blended lines
25	11	14	25	10	15	242089.1640	-0.0346	0.0300	...
25	11	15	25	10	16	242098.7040	-0.0043	0.0300	...
24	11	13	24	10	14	242884.5120	0.0257	0.0300	...
24	11	14	24	10	15	242888.6880	-0.0039	0.0300	...
23	11	12	23	10	13	243577.9080	0.0077	0.0300	...
23	11	13	23	10	14	243579.6720	-0.0094	0.0300	...
22	11	11	22	10	12	244180.5840	-0.0272	0.0300	...
22	11	12	22	10	13	244181.3400	0.0094	0.0300	...
21	11	10	21	10	11	244702.4760	0.0192	0.0300	5.0E-01
21	11	11	21	10	12	244702.4760	0.0192	0.0300	5.0E-01
20	11	9	20	10	10	245151.7200	0.0551	0.0300	5.0E-01
20	11	10	20	10	11	245151.7200	0.0551	0.0300	5.0E-01

Notes. This table and those of other isotopologues are available in their entirety in the electronic edition in the online journal: <http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/A+A/Vol/Num>. A portion is shown here for guidance regarding its form and content.